International Journal of Integrated Engineering, Vol. 8 No. 3 (2016) p. 16-20

Thermal Conductivity of Aloji Fireclay as Refractory Material

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Abstract: This investigation was concentrated on the thermal behavior and insulating property of the Aloji fireclay for its suitability of being used as refractory lining. The Aloji fireclay brick has thermal conductivity of 0.05 K (W/m.k). Heat capacity of the brick was 0.56 J/g °C at the minimum temperature of 93.33 °C as compared to 0.3 J/g °C obtained at the maximum temperature of 600 °C. The heat capacity of the clay showed that as temperature increases the heat capacity changes with phase changes. The Aloji fireclay DSC result showed a glass transition at mid-point of 554.74 °C with exothermic reaction at 510 °C as energy being released and then crystallized. The clay sample was subjected to TG+DTA analysis. The TGA result had shown that there were material weight losses of 0.076 mg, 0.25 mg and 0.52 mg at temperatures of 47.79 °C, 348.12 °C and 639.67 °C respectively. The DTA shown that there were endothermic and exothermic reactions.

Keywords: Phase change, Thermal property, Material degradation, Temperature change.

1. Introduction

Refractory material are materials that can withstand heat above 500 ˚C and contained $Al_2O_3.SiO_2.H_2O$ [1] and are often used for thermal storage in furnaces, ovens, reactors and ladles to prevent escape of heat or heat losses to the surrounding environment [2]. Furnace is the thermal equipment used for melting iron [3]. Heat losses through thermal heat storage facilities as mentioned above pose a critical problem and challenge to refractory industry that used them for their production. It is vital to search for alternative materials and means of preventing heat losses. The refractory materials used today includes; ceramic fiber glass, ceramic coating, calcium silicate, insulating castables and very recently, refractories with porosity of 10-30 % for refractory fireclay bricks and high porosity of 60-80 % for insulating refractory material [4]. The searching for alternative materials that are not only available but cheaper and health friendly can be of great advantage in resolving the challenges highlighted. Clay is naturally occurring substances that consist of fine grained minerals that become plastic when tempered with water and rigid when fired [5]. Clay of alumino-silicate group can be a better option as proposed and used in this research. This can replace glass fiber that usually posed a health challenge for the producers and users too. The use of refractory fireclay bricks around such thermal storage facilities can maintain high temperature inside such facilities and prevent heat losses to the surroundings [6]. The knowledge of thermal conductivity, energy absorption and heat capacity of these refractory materials is very necessary and critical to solving heat losses challenge. Thermal conductivity is the amount of heat conducted in a unit time through a unit area normal to the direction of heat flow [7]. Heat flow through solids is due to elastic vibration of atoms or due to transfer of energy by free electrons [8]. Heat capacity is the quantity of heat (energy) necessary to raise a major quantity of a material K and measured in J/g°C [9]. Refractory fireclay bricks have higher thermal conductivity values than insulating materials that have very low thermal conductivity values due to high porosity. They used in the construction of furnaces as refractory lining, ladles, reactors and kilns. Thermal conductivities depend entirely on the lattice vibration of atoms and molecules [10].

Nigeria is blessed with vast land, profitable solid minerals with rich and abundant clays. Clay as a raw material for production of refractories is available in commercial quantity but they remained untapped and under-utilized in the country [11]. Virtually all the refractories used in the metallurgical and other manufacturing industry are imported into Nigeria [12]. Previous researchers have shown concerned for the country's inability to utilize the abundance of these raw materials. It was observed that most investigations in this area, were on chemical and physical properties with almost nothing done through empirical research methods on thermal properties like the thermal conductivity, heat capacity and energy absorption. Research have shown that data collated on the previous work on refractory bricks materials were not detailed enough as compared to the international standard tests requirement for refractories which includes fireclay bricks [13]. Therefore, this research was aimed at investigating the Aloji fireclay to ascertain its suitability for the production of refractory material.

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2. Materials and Method

2.1 Materials

The Aloji clay used in this research was collected from Kogi state in the North central geo-political zone of Nigeria. The clay sample deposit was collected according to ASTM D4220/D4220M-14 [14] standard method of collection and transportation of soil.

2.2 Test samples preparation

Clay sample collected was sun dried for three days and the impurities were all removed. The sample clay collected was air and sun dried for three days. The clay was crushed in the ball-mill. The ASTM standard sieve mash size of 63 µm was used to sieve the clay. The specimen powder was compacted into pallets using the caver hydraulic press machine. A force of 5000 KN was applied with a holding time of 60 seconds.

2.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) equipment was loaded with 5µm of the Aloji clay sample and was placed alongside with the reference crucible in the DSC equipment with the heating rate of 5 °C per min. The energy absorption equipment have maximum temperature of 600 °C.

2.4 Thermogravimetry and Differential Thermal Analysis

A quantity of 60 mg was measured into the alumina crucible from the parent sample Aloji clay. The crucible was located inside the specimen chamber. The differential crucible was also place in the same row with the crucible containing the specimen.

2.5 Thermal shock resistance

In the thermal shock resistance test sample of size 10 mm × 50 mm × 100 mm was produced. The fireclay brick was placed in the furnace and fired at 1200 °C with the heating rate of 2.5 °C per min. It was withdrawn out from the furnace and held for 10 minutes and taken back in to the furnace. The process was repeated until a crack was noticed on the clay sample of the refractory fireclay brick surface. The last number of cycles at which the clay sample cracks was recorded as the complete cycles required for producing visible cracks in the specimen and hence, the thermal shock resistance of the fireclay brick. The determination of the thermal shock resistance was done according to ASTM C1100-88 [15].

2.6 Refractoriness

The refractoriness of the fireclay brick was investigated using the pyrometric cone equivalent (PCE) to determine the temperature of softening in order to assist in the refractory material selection that will fit the temperature of working environment. The clay sample was formed into a conical shape. The standard pyrometric cones of known softening temperatures were arranged on a standard circular shaped plaque with the aid of a suitable bonding material that will not react with the cones and thereby reducing the fusibility. The Segar cone was fixed on plaque at an angle of 82° to the horizontal. It was then placed in the heating chamber of the refractoriness testing equipment. The temperature of the equipment was raised from 27 °C to 1700 °C. Located at the top of the refractoriness testing equipment is a built in mirror that enables one to view when the clay sample bends with the corresponding Segar cone bend in the firing chamber. The moment either of these cones in the chamber bends is then the refractoriness of the fireclay brick. The experimental procedure was according to ASTM C24-89 [16].

2.7 Thermal conductivity

The thermal conductivity of the fireclay brick was determined using hot guided plate method. Test sample was prepared of circular shape of size 4 mm thick with a surface diameter of 25 mm. It was then transferred to the thermal conductivity apparatus for thermal conductivity measurement at room temperature. In the hot guided plate apparatus, the clay sample was placed in between two iron rods. Thermocouple sensors were inserted below and above the surfaces of the clay sample to observe the temperature at the lower and the upper surfaces respectively as the heat flows through the clay sample. The thermocouple was connected to the data logger; it records the temperature with respect to time. The thermal conductivity test was conducted according to ASTM C202-86 [17].

Fig. 1 Hot guided plate apparatus (steady state)

3. Results and discussion

3.1 Thermal shock resistance (TSR)

The thermal shock resistance of the Aloji fireclay was 25 cycles before it's fractured. The TSR fell within the standard values of 20-30 cycles for refractory fireclay bricks [12,15]. The fireclay fractured was as a result of temperature change caused by the interplay between the thermal expansion and thermal conductivity of the fireclay brick.

3.2 Refractoriness

The refractoriness of the fireclay brick of the Aloji clay deposit was 1665 °C which corresponded with Segar cone 30 (PCE) and was found to fall within the standard values of 1500-1700 °C for refractory fireclay bricks [11,16].

3.3 Thermal conductivity

The thermal conductivity was 0.05 K(W/m.k) and fell within the standard value of 0.01-1.1 K(W/m.k) for refractory fireclay bricks [7-9]. The thermal conductivity was obtained as a result of the atomic and lattice vibration which is impeded via structural disorder. Temperature gradient determines the direction of heat flow:

$$\frac{Q}{A} = K = \frac{\Delta T}{\Delta X} \qquad (1)$$

Therefore, thermal conductivity will drop with increasing temperature.

3.4 Specific heat capacity

Specific heat capacity of Aloji fireclay brick as presented in Figure 3 was 0.56 J/g °C at the minimum temperature of 93.33 °C as compared to the lowest value of 0.3 J/g°C obtained at the maximum temperature of 600 °C. Specific heat capacity affect the internal energy of the brick which causes the molecules to be in motion and make its particles vibrate faster, collide more violently thereby increasing the bulk density of the refractory brick. The result shown that the effect of specific heat capacity was on the thermal conductivity of the clay particles, porosity and on the removal of moisture content from the fireclay brick. The heat capacity of the clay showed that as temperature increases the heat capacity changes with phase changes [8,9].

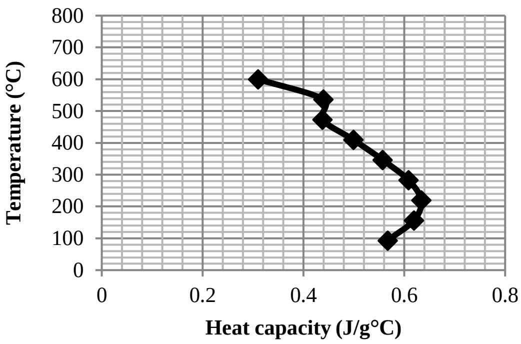

Fig. 2 Specific heat capacity of Aloji fireclay

3.5 Energy absorption

Differential scanning calorimetry (DSC) was used to investigate the difference in the quantity of heat necessary to increase the temperature of a specimen and reference is measured as a function of temperature. The Aloji fireclay showed that as the temperature increases the clay sample developed phase change with sizable energy absorption. The equipment differential scanning calorimetry had maximum heat capacity of 600 J/°C (DSC). The Aloji fireclay as presented in Table 1 and Fig. 3 showed a glass transition at mid-point of 554.74 °C with exothermic reaction at 510 °C of energy being released and then crystallized. The study is similar to the work of Johari *et al.* (2010) [18].

Table 1 DSC result indicating the glass transition, reaction and specific heat capacity

Enthalpy (°C)	Jg-1	C_P (J/g°C)	Glass transition mid-point (°C)	Onset (°C)	Reaction
29.99	0	0	554.74	537.12	Exo-thermic
93.33	52.93	0.56713			
156.67	97.02	0.61926			
220.02	139.38	0.63349			
283.36	172.27	0.60796			
346.71	193.05	0.55681			
410.05	204.55	0.49884			
473.4	207.04	0.43735			
536.74	235.75	0.43923			
600.08	186.02	0.30999			

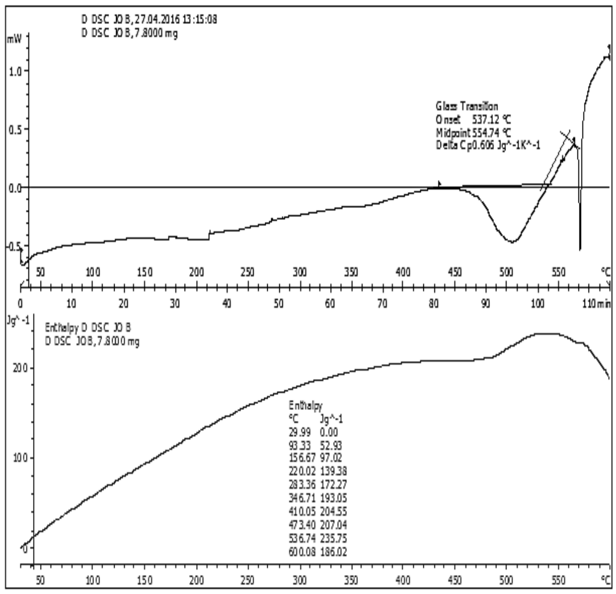

Fig. 3 Energy absorption (Enthalpy)

3.6 Thermal analysis (TG+DTA)

In the thermogravimetric (TGA), the Aloji fireclay as graphically presented in Fig. 4 showed that at temperature of 47.79 °C the clay sample experienced material reduction of 0.076 mg representing 0.127 %.

This signified the evaporation of water in the material. At the temperature of 348.21 °C the material exhibited further reduction of 0.028 mg representing 0.30 %. This showed that the molecular structure of the clay was affected by the temperatures above 300-350 °C and carbonaceous material in the clay has decomposed and as such caused material reduction. At the temperature of 639.67 °C there was material reduction of 0.52 mg which represented 0.44 %. The effect of TGA was seen to cause fireclay refractory brick sample to weight loss, while DTA caused exothermic reaction in the refractory brick sample as energy being released and endothermic reaction in the refractory brick as absorbed energy. The dehydroxylation of the minerals in the clay ensues at these temperatures. It signified the initial step in the oxidative degradation of the clay material. The flux compounds like P_2O_5, CaO and K_2O manifested reaction from 900 °C which signified the beginning of sintering process, material crystallization and phase change. The differential thermal analysis (DTA) as presented graphically in Fig. 5 showed an indication that the clay specimen experienced endothermic reactions at temperatures of 62.92 °C and 450 °C respectively. This means the clay material releases energy to its environment. The final reaction exhibited by the clay was exothermic at the temperature of 1215 °C. This means that the clay absorbed some energy at that particular temperature. The TG+DTA were similar to the research work of Johari *et al.* [18] and Gregia *et al*. [19].

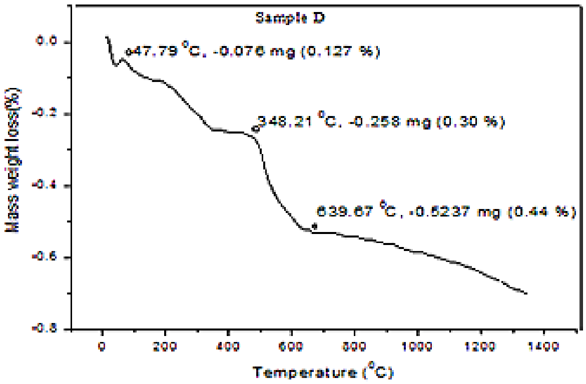

Fig. 4 TGA curve for Aloji fireclay brick

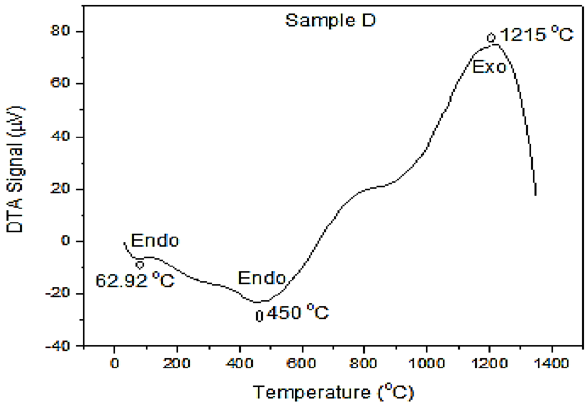

Fig. 5 DTA graph of Aloji fireclay brick

4. Conclusion

The Aloji fireclay based on the results of thermal conductivity value of 0.05 K(W/m.k), the specific heat capacity changes with change in temperature, the refractoriness (PCE) was 1665 °C, Thermal shock resistance was 25 cycles, DSC, TGA and DTA was found to be within the standard values for refractory fireclay bricks, hence, they are suitable for production of refractory fireclay brick for furnace lining.

Acknowledgements

The authors would like to acknowledge Universiti Tun Hussein Onn Malaysia, Centre for Graduate Studies, ORICC for the Graduate Research Incentive Grant (Vot No: U293) and Faculty of Mechanical and Manufacturing Engineering.

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